

Catalysts via First Principles

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**DOE VEHICLE TECHNOLOGIES
PROGRAM ANNUAL MERIT
REVIEW, FY 2013**

Project PM050

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Collaborators

- **ORNL**

- M.M Debusk (supported catalyst – staff at ORNL)
- Xiaofan Yang (NH₃-SCR catalyst - now at BASF)
- G.M Stocks (Theory)
- M. Yoon (Theory)
- L.F. Allard (ACEM of supported Pt)
- A. Lupini and S. Penneycook (ACEM of Pt-Pd)
- D.R. Mullins (EXAFS & XANES)
- S.M. Mahurin (EPR)
- M. Kidder (UV-VIS)

- **John Deere Power System**

- D. Dou
- A.Kozlov
 - Completed WFO on urea-SCR catalyst
 - Protocols for degreening, hydrothermal aging, and testing for off-road conditions
 - Guiding commercialization

Overview

Timeline

- Start: Oct. 2004
- Finish: Sep. 2014

Budget

- Funding received in 2012
 - \$300K
- Funding authorized in 2013
 - \$300K

Barriers

- Changing internal combustion engine combustion regimes
- Cost and durability of emission control systems
- Long lead times for materials commercialization
- Many advanced vehicle technologies rely on materials with limited domestic supplies

Partners

- Collaboration with John Deere
 - Completed work-for-others arrangement on NO_x treatment
- Presentation to USCAR
 - Interest from Chrysler, Cummins, and SWRI

Objectives

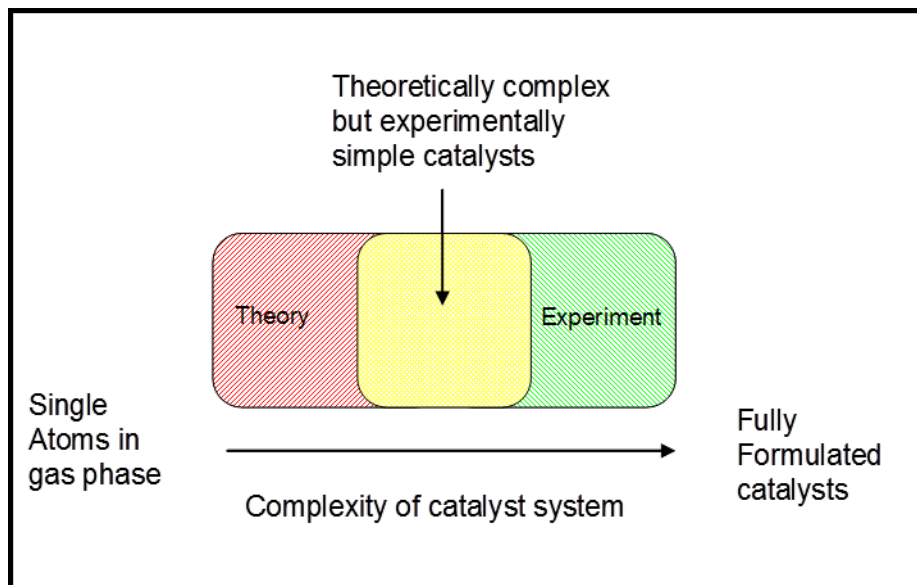
- Demonstrate that we can investigate catalyst systems by first principle theoretical models, experimental studies, and nanostructural characterization iteratively to forecast improvements to obtain optimum catalyst systems
- Identify optimum catalyst sites and develop **durable, reliable, well-characterized** catalyst materials
- Emission treatment catalysts that work even at temperatures as low as 150°C

Barriers - Relevance

- Changing internal combustion engine regimes – lower exhaust temperatures – challenges to catalysis. Cost, durability, and long lead time.
 - Advances in emission catalysts from trial and error method
 - Although successful, very time consuming, resource intensive
 - In recent years, nanostructural characterization of catalysts has been helpful in advancing the state-of-the-research in emission catalysts
 - Provides information on gradual but persistent decrease in catalyst performance (e.g. catalyst coarsening, noble metal migration, changes in support etc.)
 - But, does not offer approaches to alleviate the problem
 - Theoretical studies were limited to gas-phase or very simple systems
 - Not adequate towards design of complex catalyst system
- Can we benefit from the advances in catalyst synthesis, theory, and nanostructural characterization to better understand catalyst sites and reduce the iterations in emission catalyst design?
- Can our work lead to catalysts that are active at low temperatures ($\sim 150^{\circ}\text{C}$)?

Approach

Supported clusters (Pt, Rh) are integral part of vehicle emission treatment catalysts such as oxidation catalyst, three-way catalyst, lean NO_x traps, diesel particulate filters. For lean burn NO_x treatment, urea-selective catalytic reduction (SCR) is currently leading technology and is based on zeolites.



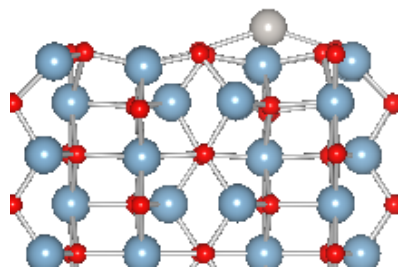
- Theoretical Modeling
 - First Principles modeling of Pt clusters on oxide supports
 - Zeolite catalysts
 - Interaction of CO, NO_x, and HC with catalysts
- Experimental System
 - Synthesis of Pt Nanoclusters on morphologically diverse oxide supports
 - Interaction of CO, NO_x, and HC with catalysts
 - Zeolite catalysts for SCR
- Structure
 - Nano-structural characterization

C.K. Narula, "Catalyst by Design", Encyclopedia of Nanoscience and Nanotechnology, Taylor & Francis, New York, 2008, pp 771-782.

Theory on realistic catalyst (Pt/Alumina)

We have determined that θ -alumina is a better surrogate for γ -alumina than α -alumina

- Platinum occupies a position between two surface oxygen atoms of θ -alumina



Pt on θ -Al₂O₃ (010) Surface

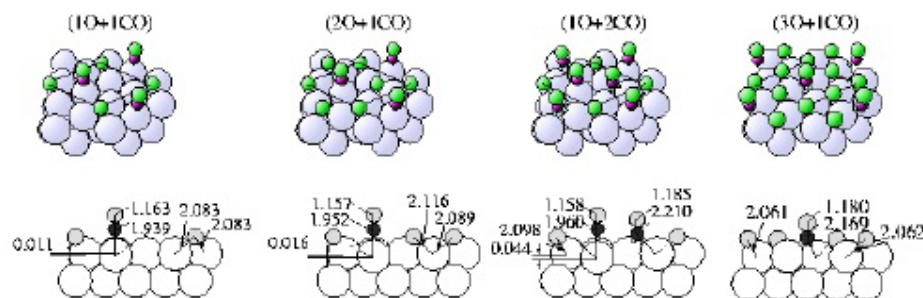
- The adsorbed Pt is in d¹⁰
- Pt-O distances are larger than Pt-O bond distances calculated for Pt-O cluster in gas-phase (1.76 Å) or Pt/ α -alumina (2.0 Å) but are closer to bulk Pt-O (2.08 Å)
- Isoelectronic with (Ph₃P)₂Pt – should be catalytically active

C.K. Narula, G.M. Stocks, J. Phys. Chem. C, 2012, 116, 5628

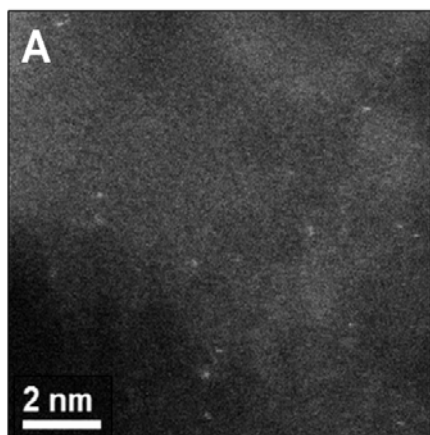
- This structure is different from Pt/ α -Alumina where Pt atom is atop surface oxygen and

- Calculated Pt-O distance is 2.02Å. The adsorbed platinum atom is d⁹
- The interaction of Pt with surface is summarized as localized covalent bonding between Pt and O enabled by nearly Al-centered electron-accepting empty states available to accept excess electron density

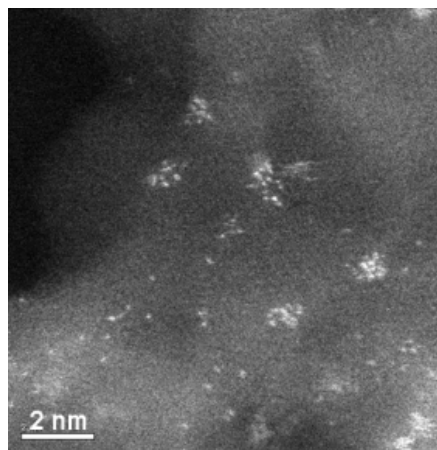
- Can we make monodisperse single atom Pt/ θ -alumina?
- Will it be catalytically active?
- If yes, what is the mechanism?



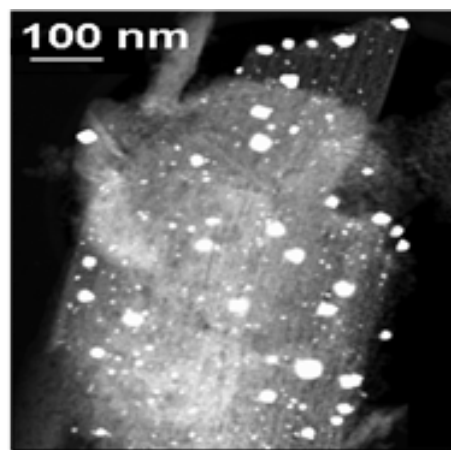
Single Supported Pt atoms – we can make it and it is catalytically active



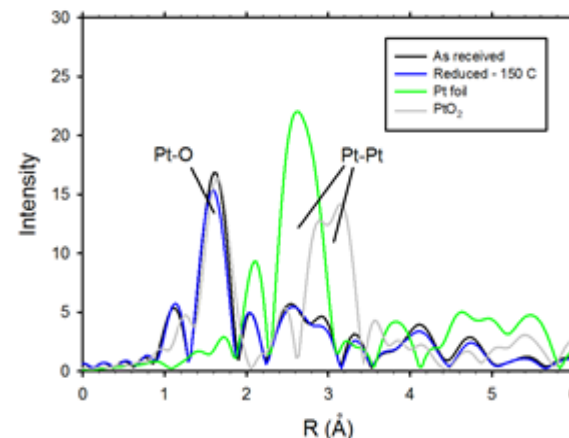
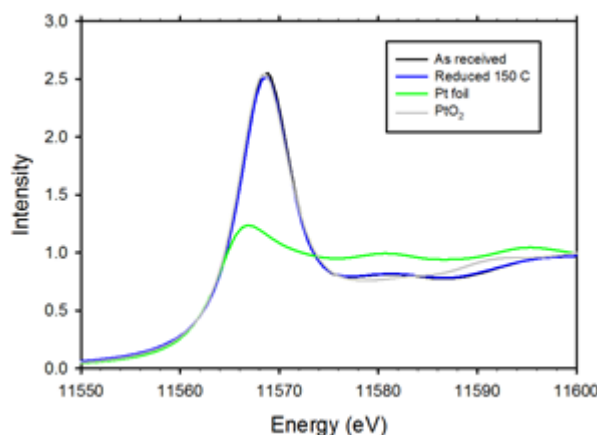
0.18% Pt/θ-alumina



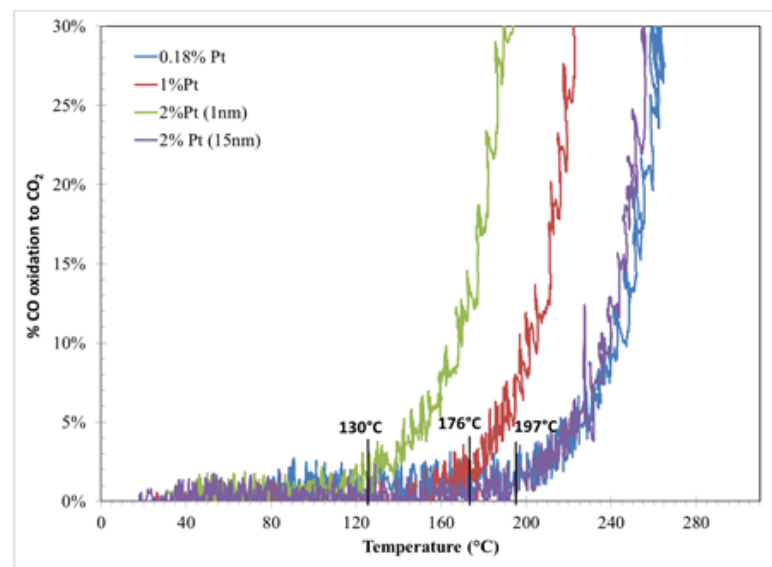
1.0% Pt/θ-alumina



2.0% Pt/θ-alumina-650°C



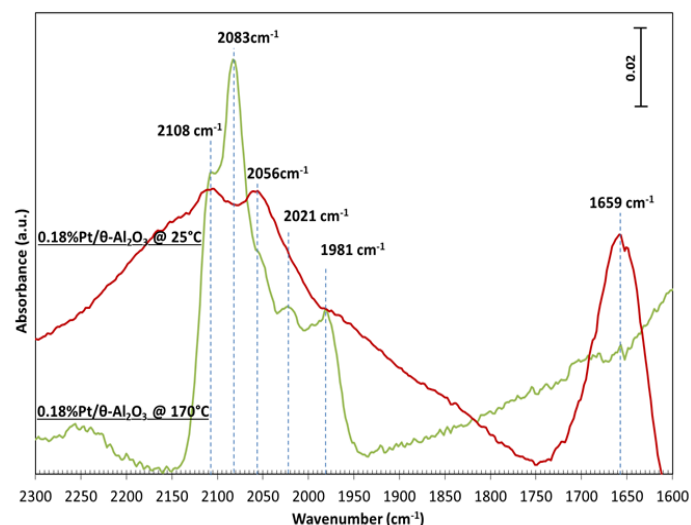
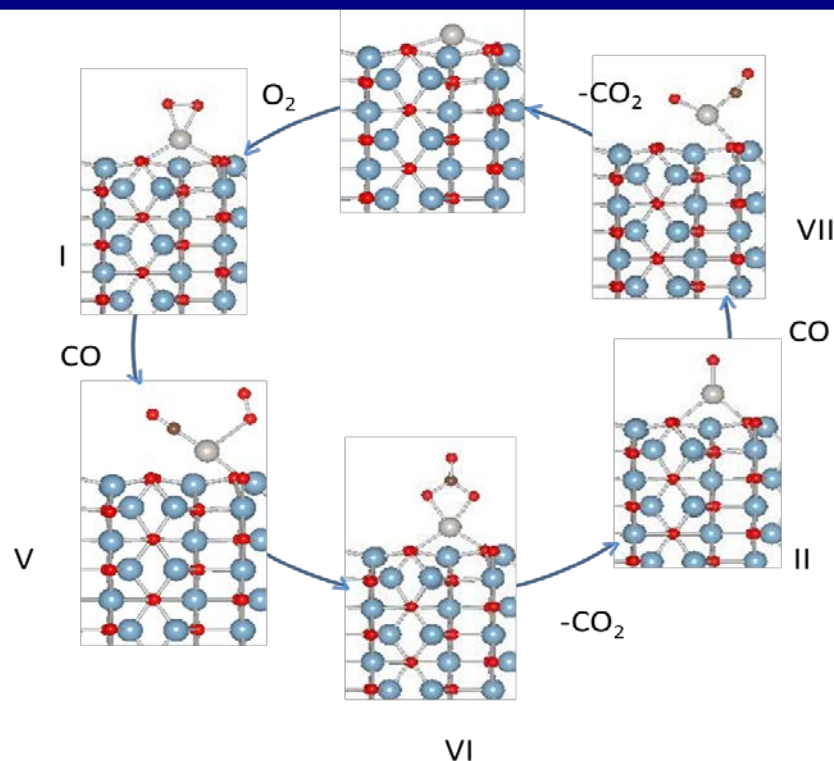
XANES & EXAFS of single Pt atoms on θ-alumina



CO oxidation on Pt/θ-alumina

What is the mechanism?

Proposed new mechanism of CO oxidation supported by experiments

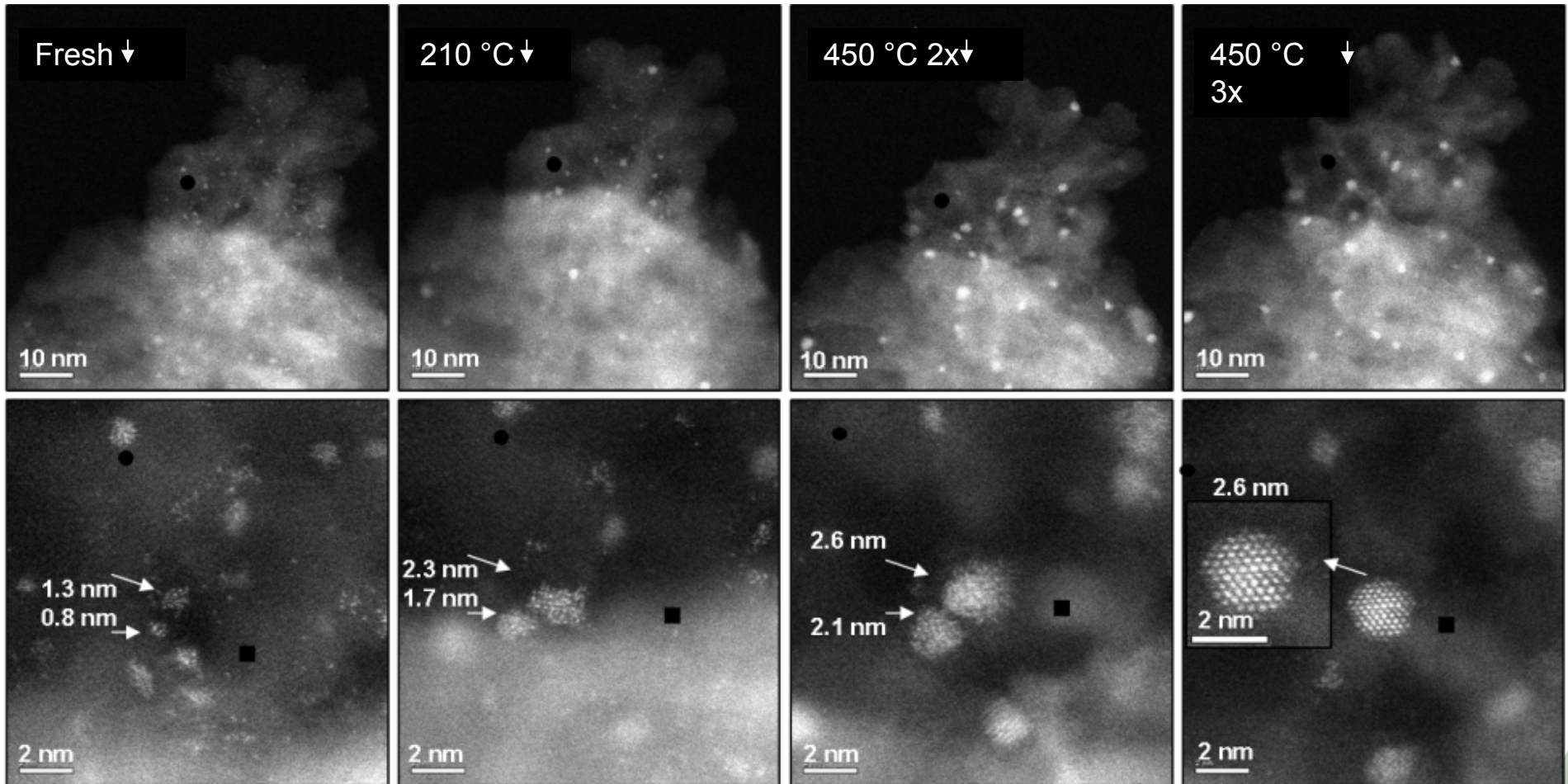


- Inspired by organometallic chemistry
- Analogues of I and VI in organometallic chemistry have been isolated
 - (Ph₃P)₂Pt(O₂)
 - (Ph₃P)₂Pt(CO₃)
- All steps are energetically favored except carbonate dissociation to II which is endothermic
 - Surface will get covered with CO₃
- DRIFTS studies of CO absorption show CO₃ formation

C.K. Narula et. al., J. Am. Chem. Soc., submitted

ACEM HAADF-STEM images Pt particle growth of the exact same sample area after exposure to CO-Oxidation conditions

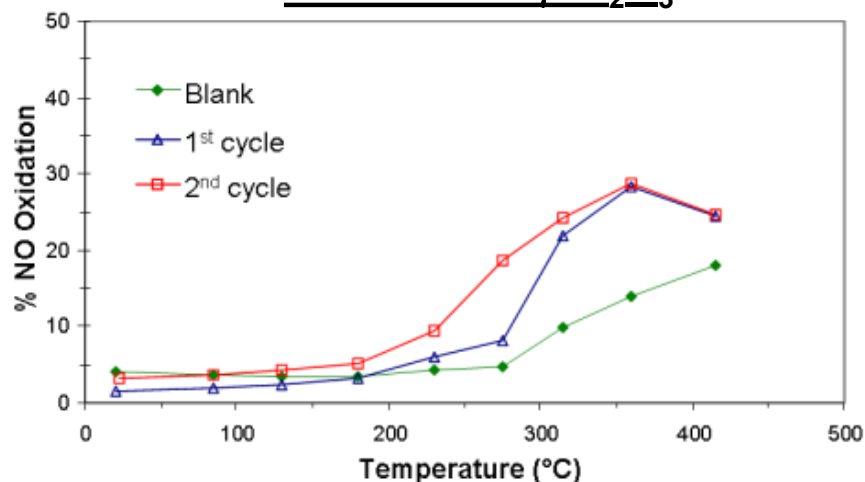
Ex-situ Reactor Studies



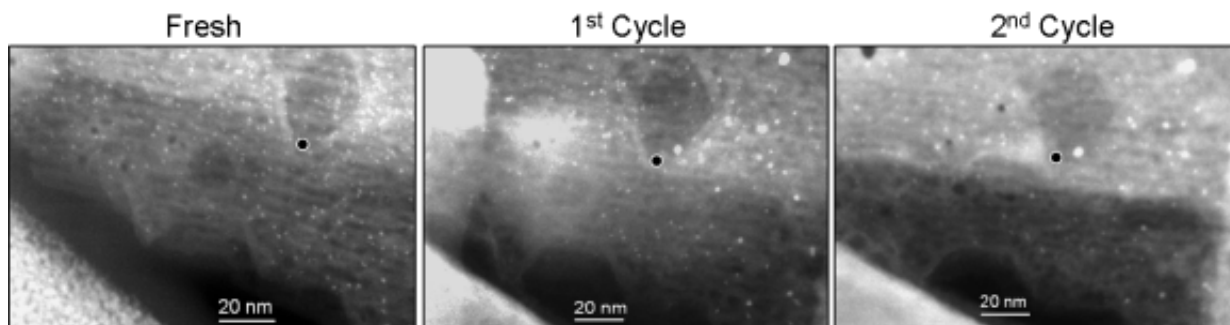
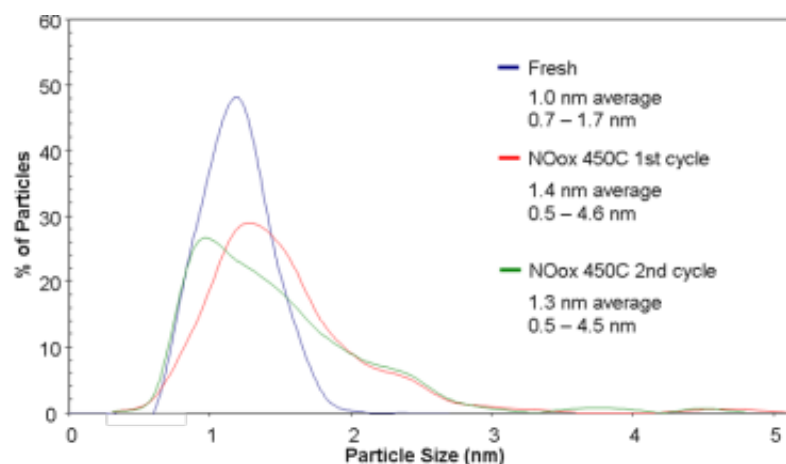
Rapid growth in Pt particles can be followed as a function of CO-oxidation conditions

NO Oxidation is not very effective on Pt single atoms and nanoparticles

1 nm 2% Pt/ γ -Al₂O₃

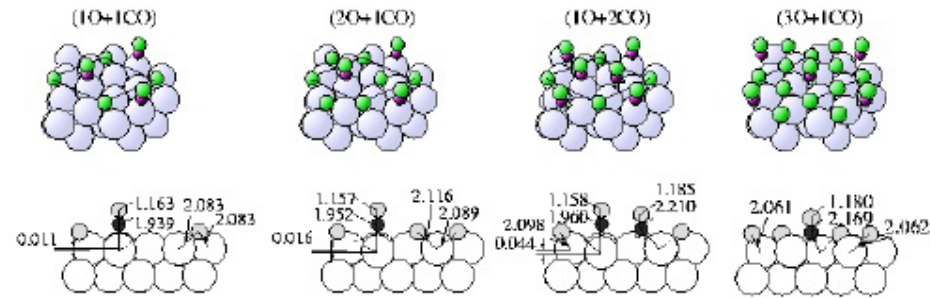


- A 500 ppm mixture of NO with 10% O₂ and balance N₂ at ~50k h⁻¹ space velocity
- The 2nd cycle initiates at a lower temperature than the 1st cycle



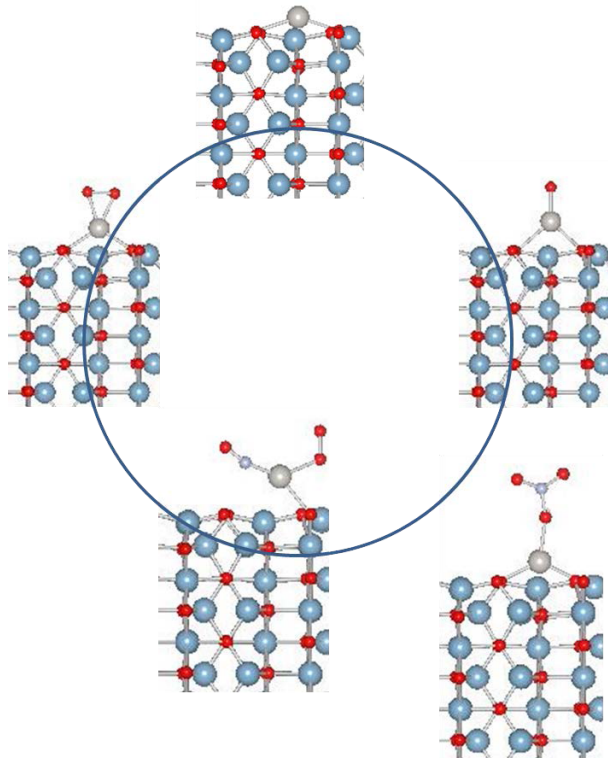
- Results of *ex-situ* studies suggest that the average particles size under these conditions is not effected but the particle size range increases. Since the fresh sample has already been calcined at 450°C/5h prior to testing, the sintering observed in the *ex-situ* studies can be primarily contributed to the NO oxidation environment.

Mechanism explains why NO oxidation is less effective on single atoms and nanoparticle



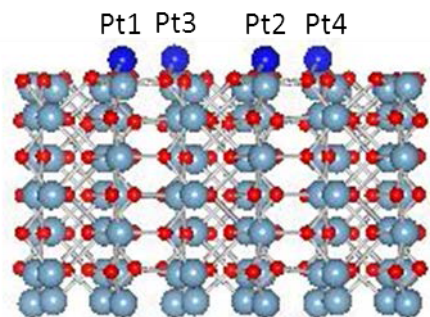
NO oxidation on Pt particles

- Pathway analogous to the proposed pathway for CO oxidation
- Unlike carbonate formation, NO_3 formation is energetically not favored
- Explains poor NO oxidation on nanoparticles.

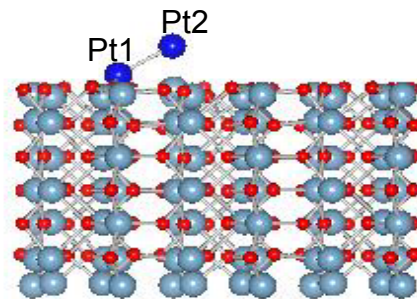


1.1 eV higher in energy

Pt Clusters – Missing 2-10 atoms clusters and driving force for sintering

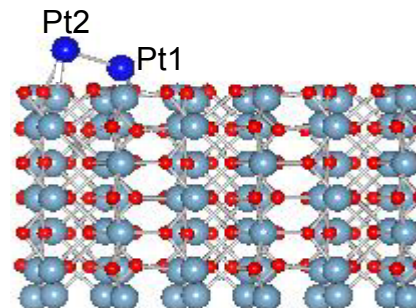


Pt2 -3047.5495 eV
 Pt3 -3051.1554 eV
 Pt4 -3054.4954 eV
 d¹⁰ species

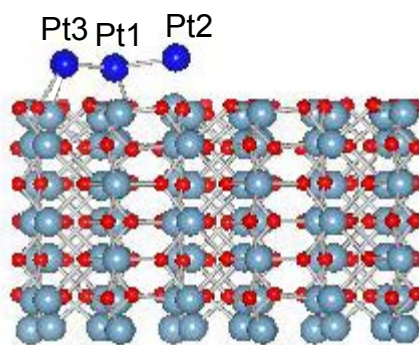


-3047.8793 eV
 d¹⁰ species

Pt2

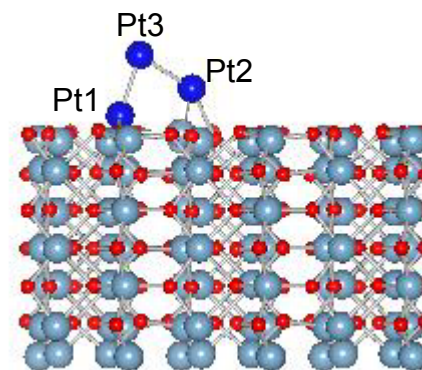


-3047.7091 eV
 d⁹ species

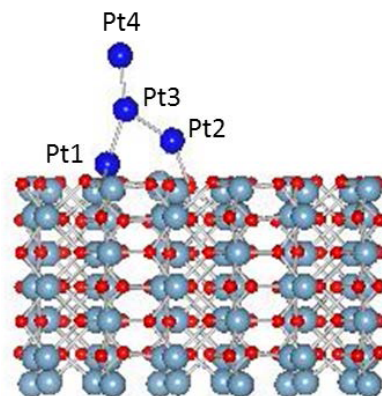


-3053.0851 eV
 d⁹ species

Pt3



-3052.0431 eV
 d⁹ species



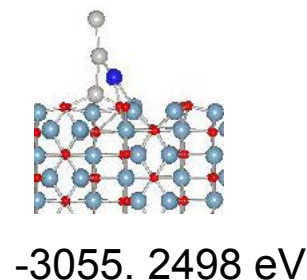
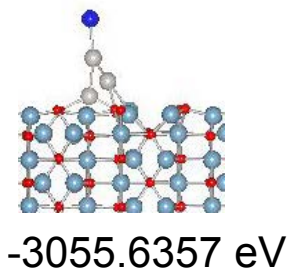
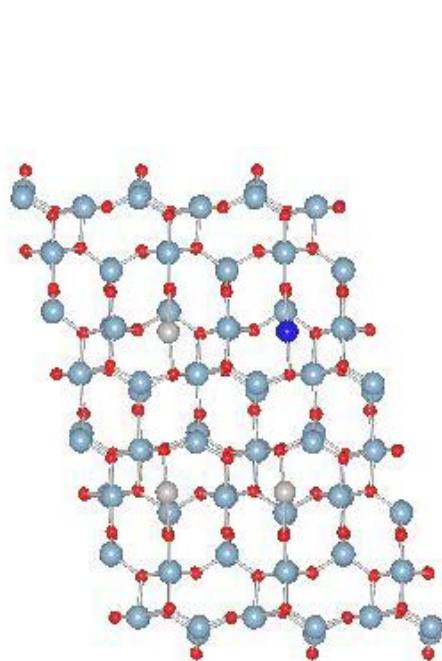
-3057.8930 eV
 d¹⁰ species

Pt4

Energetics favor agglomeration

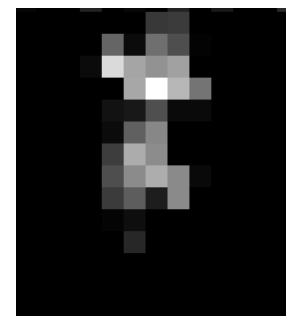
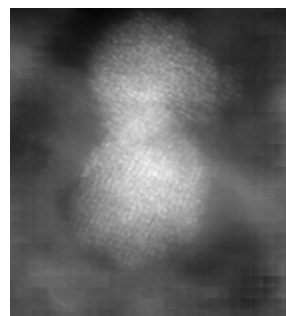
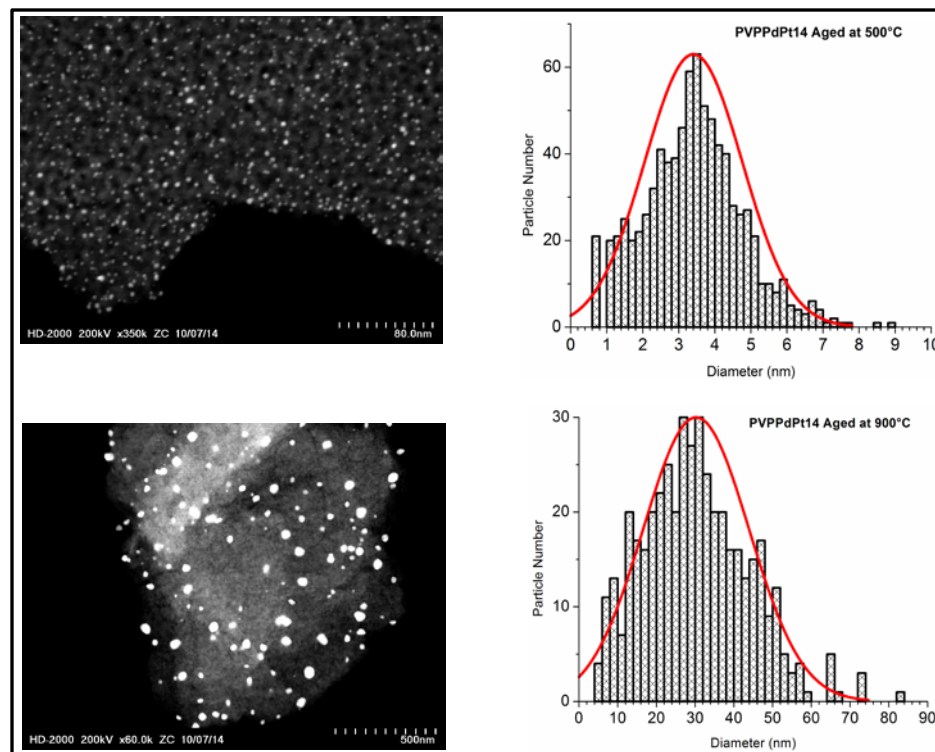
Explanation of Stability of Pt-Pd/Alumina

Insights from single atom and small clusters studies allowed us to investigate Pt-Pd clusters



-3054.4628 eV
MM = 0
 d^{10} species

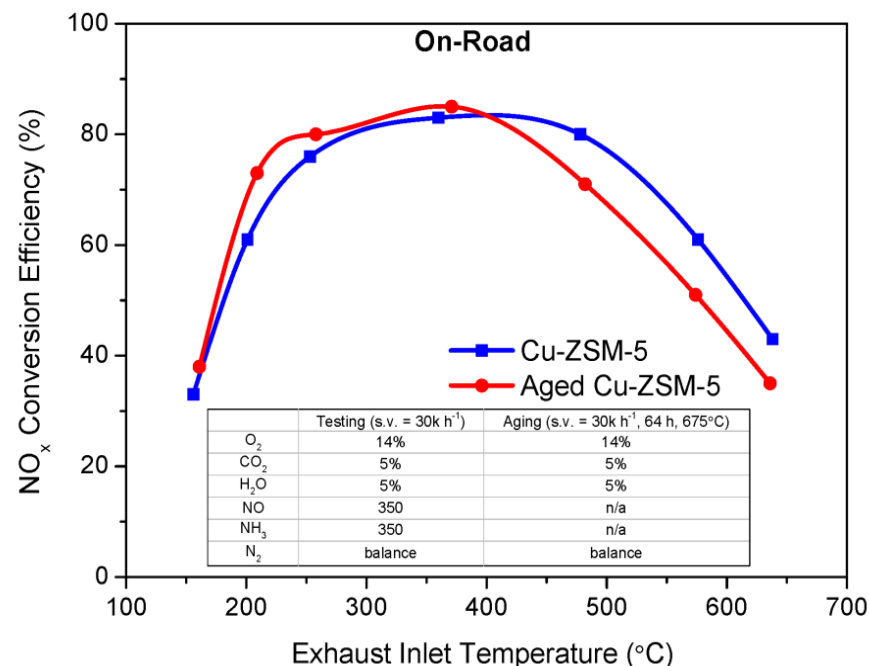
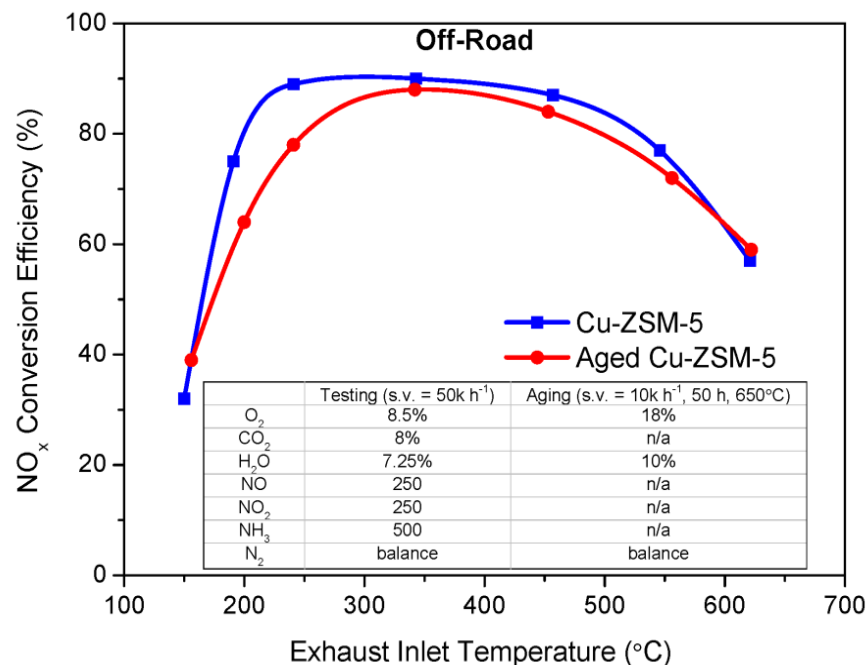
Narula, C.K.; et al., To be published.



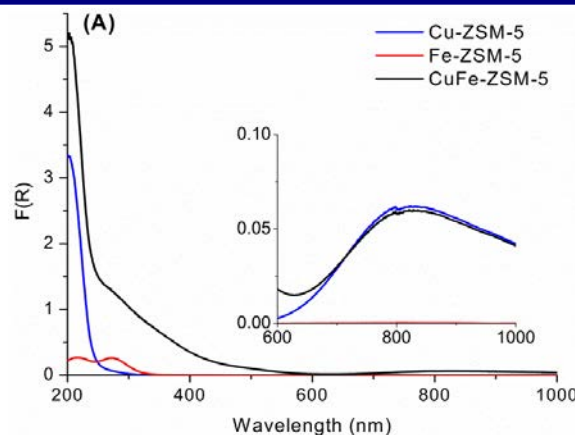
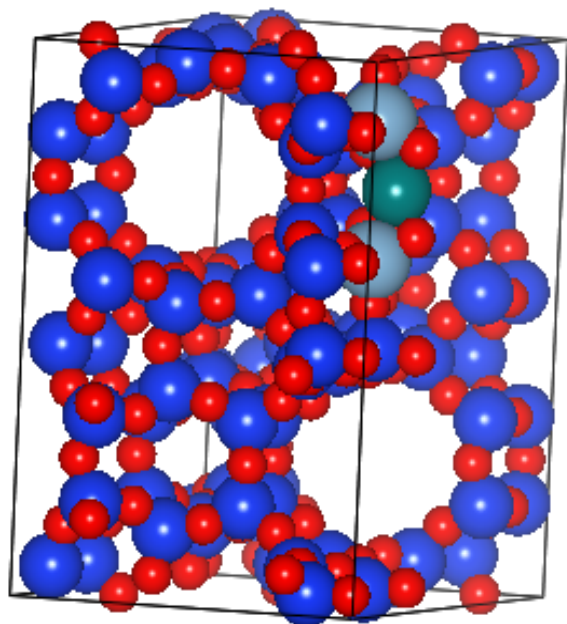
- No 300-400 nm particles normally seen for supported Pt after hydrothermal aging
- Particles sinter with Pd opening the shell to allow core Pt to combine. **Pd controls durability!**
- Theoretical studies to find alternates to Pd in progress

Development of Hydrothermally stable catalyst for NO_x Treatment from Off-Road Diesel Engines that works at 150°C

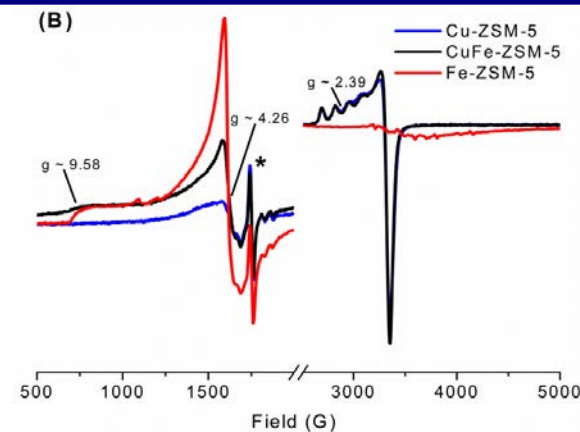
- We initiated our research by employing Cu-ZSM-5 which has been shown to be highly effective NH₃-SCR catalysts for passenger vehicles.
- Cu-ZSM-5 displayed a operating temperature window of 200-550°C for NO_x conversion.



ZSM-5 was employed as a model for developing new heterobimetallic zeolites

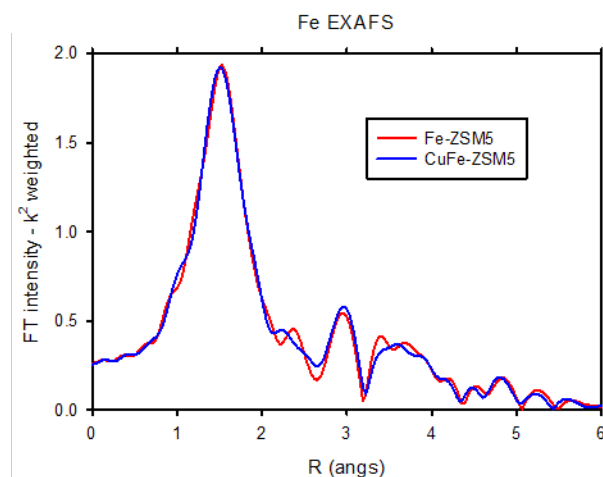
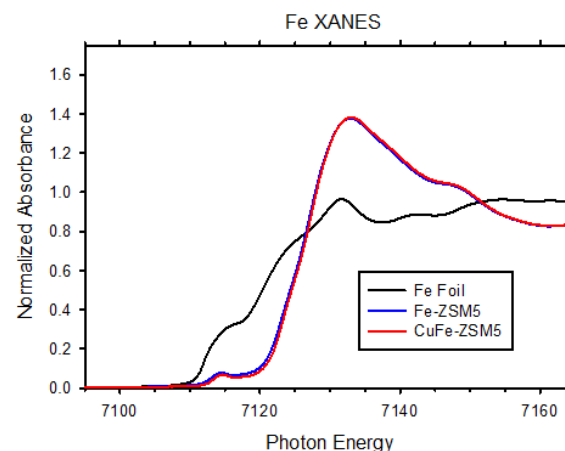


UV-VIS of CuFe-ZSM-5 shows 210 and 270 nm peaks for Fe-O-Fe clusters



EPR of CuFe-ZSM-5 is identical to that of Cu-ZSM-5 except increase in intensity of signal at $g \sim 4.3$ due to Fe^{3+}

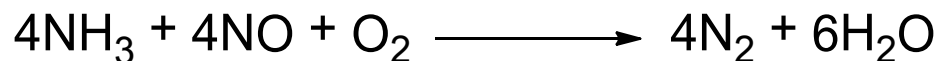
- **CuFe-ZSM-5 – Adding iron to Cu-ZSM-5**
- **Method I: Exchange of Cu-ZSM-5 with dilute $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ at 80°C, separation, and pyrolysis at 500°C**
- **Method II: New approach incipient wetness – metal nitrate in water to coat Cu-ZSM-5. Pyrolysis at 500°C.**



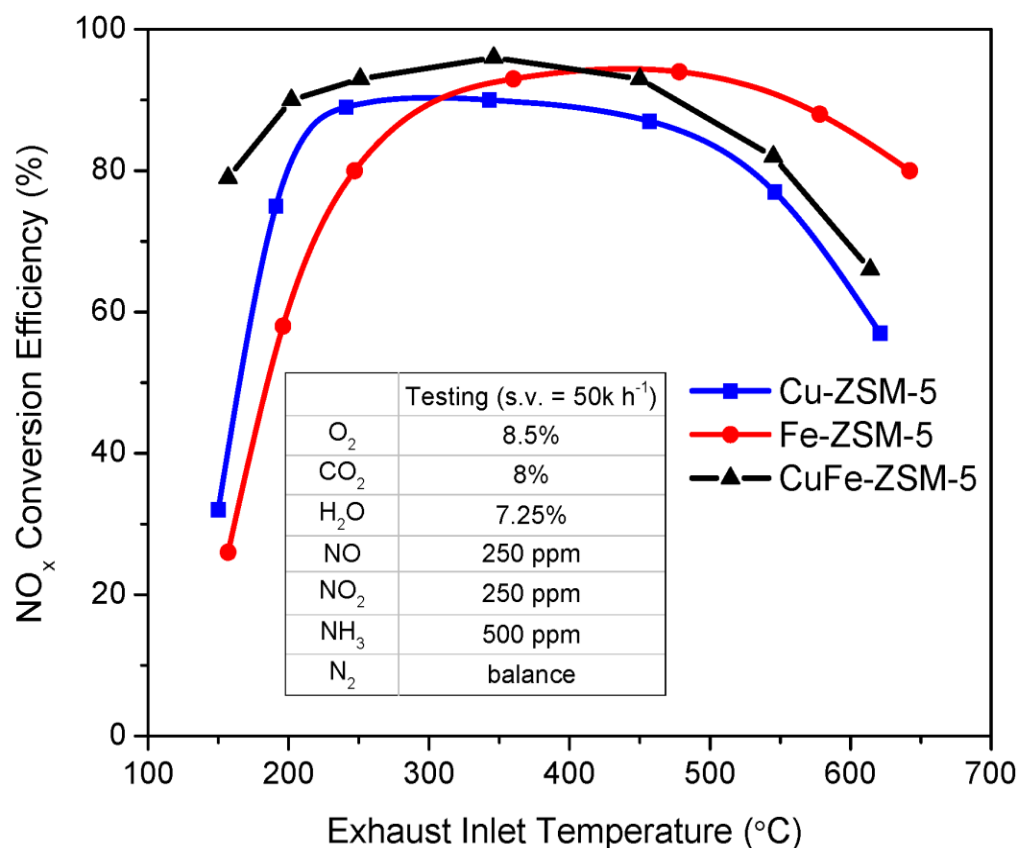
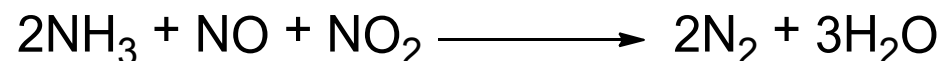
Fe-EXAFS and Fe-XANES are similar to that of Fe-ZSM-5 but show Fe-Metal interaction at 2.0-3.5 Å assigned to iron oxo dimers

CuFe-ZSM-5 – New Low Temperature NH₃-SCR Catalysts – 80% NO_x conversion at 150°C

a). Standard SCR reaction



b). Fast SCR reaction

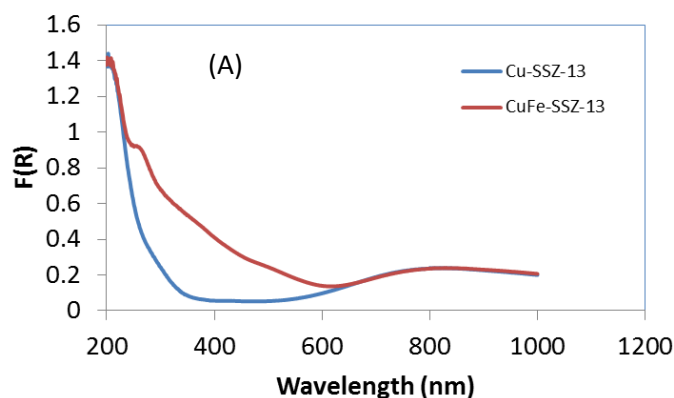
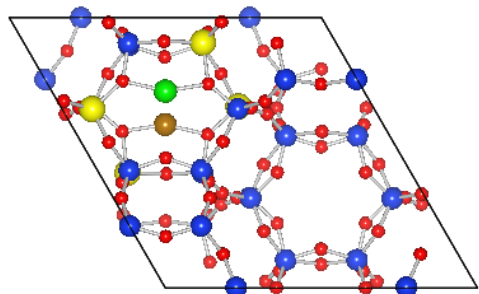


➤ Cu-ZSM-5 and Fe-ZSM-5 are synthesized using literature procedures.

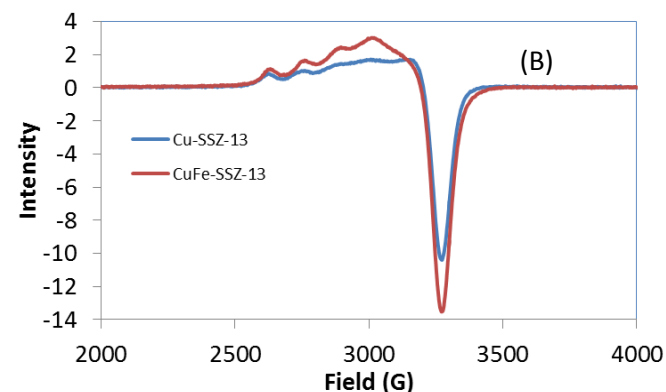
➤ Off-road degreening and testing protocols are provided by John-Deer Power System.

➤ CuFe-ZSM-5 shows **remarkable low temperature reactivity**, outperforming the mechanical mixture of Cu-ZSM-5 and Fe-ZSM-5. CuIn-ZSM-5 and Cu-Sc-ZSM-5 equally good.

Modifying commercial (Chabazites) catalyst to incorporate Fe

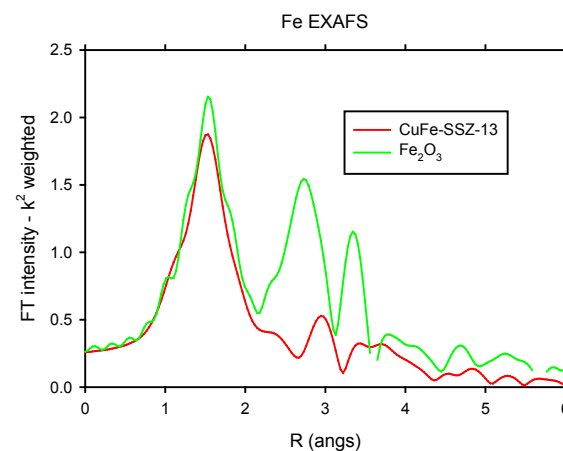
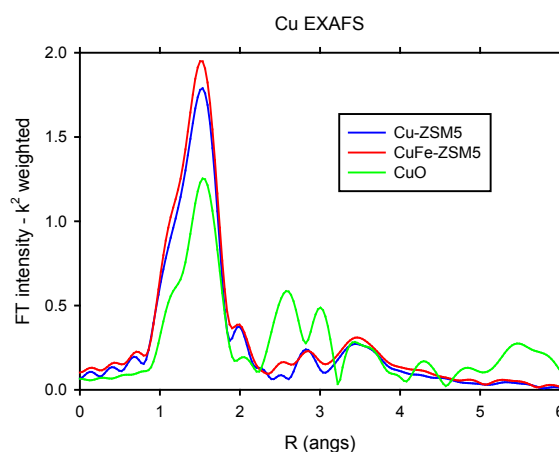


UV-VIS of CuFe-SSZ-13 shows 210 and 270 nm peaks for Fe-O-Fe clusters



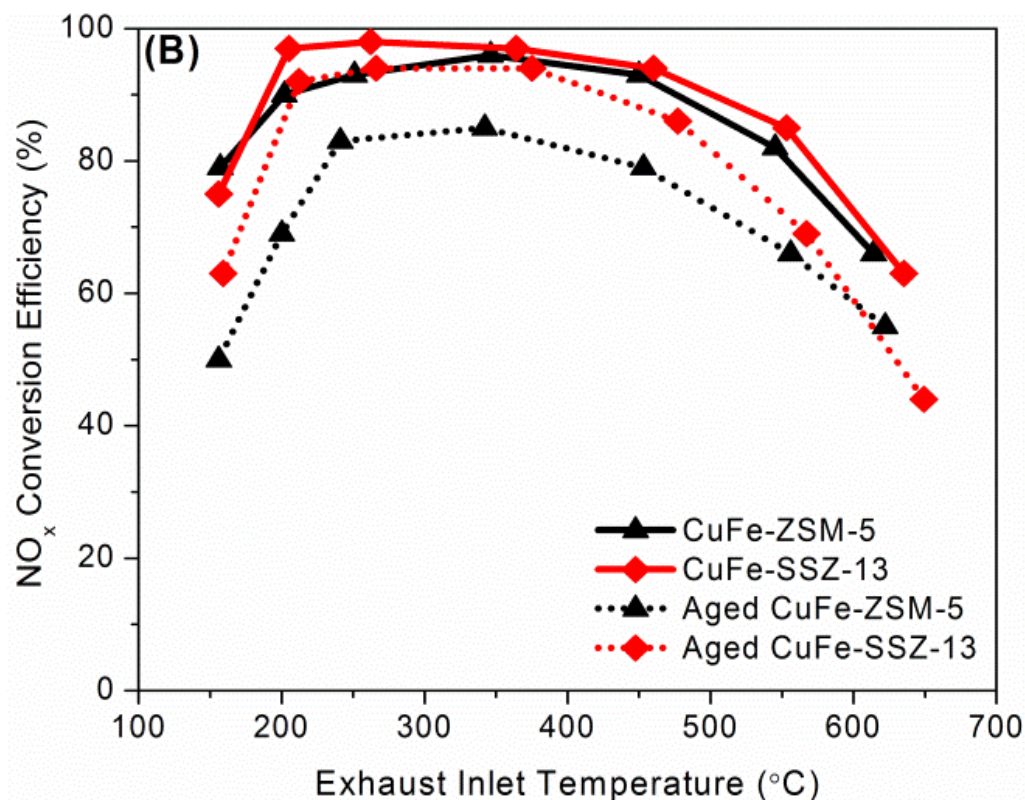
EPR of CuFe-SSZ-13 is identical to that of Cu-SSZ-13

- **CuFe-SSZ-13 – Adding iron to Cu-ZSM-5**
- **Method I: Exchange of Cu-SSZ-13 with dilute $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ at 80°C, separation, and pyrolysis at 500C**
- **Method II: New approach incipient wetness – metal nitrate in water to coat Cu-SSZ-13. Pyrolysis at 500C.**



Fe-Metal interaction at 2.0-3.5Å assigned to iron oxo dimers

Modified commercial catalyst CuFe-SSZ-13 converts 80% NO_x at 150°C and is hydrothermally stable



➤ CuFe-SSZ-13 shows remarkable low temperature reactivity.

➤ CuFe-SSZ-13 is hydrothermally stable when tested after subjecting to accelerated aging protocol

➤ Both objectives achieved – hydrothermal durability and NO_x activity at 150°C in laboratory for fast SCR

Preparing for engine testing in FY13

Collaboration

- Technology Transfer
 - Collaboration with Dr. Danan Dou and Dr. Alex Kozlov of John Deere
 - Completed work-for-others arrangement on NO_x treatment for off-road vehicles
 - Completed jointly funded project on NO_x treatment from DOE-ITP office from FY08-FY12
- Engine Tests
 - Support from John Deere
 - Inquiry from Southwest Research Institute®
 - Presentation to USCAR
 - Expression of interest from Chrysler and Cummins

Summary

- Relevance: Low temperature catalysts are needed due to Changing internal combustion engine regimes – lower exhaust temperatures
- Approach: We employ “catalyst by design” approach for speeding up the discovery process
- Collaborations: John Deere Power System, Chrysler, Cummins, & SWRI® expressed interest as we move towards engine testing.
- Technical Accomplishments
 - Demonstrated hydrothermally stable NH_3 -SCR heterobimetallic zeolites that reduce NO_x effectively at 150°C .
 - Developed understanding of agglomeration and explained the basis for Pd-Pt hydrothermal stability to facilitate search for low cost platinum stabilizer
 - For the first time showed Pt single atoms are catalytically active for CO but not for NO_x – Impact on catalyst design.
- Future Work:
 - Prepare for Engine Tests of NH_3 -SCR catalyst
 - Explore low cost alternatives to palladium for Pt stabilization

Activities for Next Year

- SCR catalyst
 - Theoretical studies to understand the role of heteroatom
 - Methods to modify commercial urea-SCR catalysts
 - Engine Testing
- Bimetallic systems to alleviate Pt sintering – progress towards low temperature supported catalyst
 - Theoretical studies
 - Synthesis of sub nanometer particles

Acknowledgements

- This research was sponsored by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Office of Vehicle Technologies under Propulsion Materials Program under contract DE-AC05-00OR22725 with UT-Battelle, LLC.
- Computation work in part (M.G. Stocks) is supported by Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, US Department of Energy.
- A portion of this research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Division of Scientific User Facilities, U.S. Department of Energy.
- Early work on heterobimetallic zeolites was supported by Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office.
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- J. Gibbs, Technology Development Manager